PRINCE OF SONGKLA UNIVERSITY

FACULTY OF ENGINEERING

Midterm Examination : Semester I | Academic Year : 2006

Date : 5 August 2006 | Time : 09.00 – 12.00

Subject : 230 - 463 Polymer Technology | Room : A400

Student Name: ..... ID no. : .....

Number of questions : 5

Time : 3 hours

Total marks : 110

Notes are not allowed

Calculators are allowed

Question	Full Marks	Marks Received
1	15	
2	25	
3	25	
4	20	
5	25	
Total	110	

ทุจริตในการสอบโทษขั้นต่ำคือ ปรับตกในรายวิชาที่ทุจริต และพักการเรียน 1 ภาคการศึกษา

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1. a) Write the repeating units of the following polymers: polyester, polyamide, polystyrene and poly methyl methacrylate.
   b) Explain the meaning of a structural unit in a step polymer.
   c) Explain the number fraction of x-mer in linear step-polymers in terms of structural units.
   d) For linear step polymers, the number distribution and the weight distribution of x-mers are given by:

$$N_x^* = p^{x-1}(1-p)$$

$$w_x = x(1-p)^2 p^{x-1}$$

where N_x^* = number fraction of x-mer

w_x = weight fraction of x-mer

Plot w_x against x for p =0.92 and 0.97.

Compare and explain the effects of p on molecular weight.

(15 marks)

Answer to Q1

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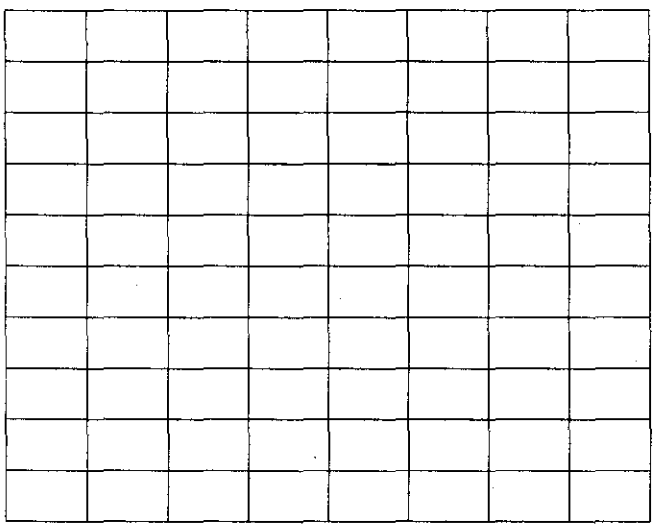
Answer to Q1.(continued)

Q1d)

Graph for plot of distribution curves



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2. a) In the stepwise polymerization of two monomers adipic acid, HOOC-$(CH_2)_4$-COOH and ethylene glycol, HO-$(CH_2)_2$-OH it was planned to add both reactants in stoichiometric amount. If the adipic acid contains 2% monocarboxylic acid, calculate the $\bar{x}_n$ and $\bar{M}_n$ of the polymer formed when p =1.0.

Note that:

In the reaction of monomer types A-A and B-B with an excess of functional group type B the number-average degree of polymerization is given by

$$\bar{x}_n = \frac{1+r}{1+r-2rp}$$

where r = ratio of the functional types in which $r \leq 1$

p = extent of reaction of the functional group type A

(10 marks)

b) A polymerization system contains of 1 mol of a diol, 2 mol of triol and 4 mol of diacid.

2b.1 Calculate gelation by reaction stoichiometry. Note that:

$$p = \frac{2}{f_{av}} - \frac{2}{\bar{X}_n f_{av}}$$

2b.2 Calculate gelation by statistics and branching coefficient, α_c.

Note that:

$$\alpha_c = \frac{1}{(f-1)} = \frac{rp_c^2\rho}{1 - rp_c^2(1-\rho)}$$

f = functionality of the branch unit

$$\rho = \frac{\text{Number of F.G. type A in branch unit}}{\text{Number of F.G. type A in reaction mixture}}$$

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$$r = \frac{\text{All number of F.G. type A}}{\text{All number of F.G. type B}} = \frac{N_A}{N_B}$$

2b.3 Compare and comment on the values obtained in 2b.1 and 2b.2.

(15 marks)

Answer to Q2.

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3. One hundred litres of acrylonitrile is bulk polymerized at 60°C with 4 g of dibenzoyl peroxide. The density of liquid acrylonitrile monomer is 0.8 g/cm^3 and its molecular weight is 53 g/mole. The density and molecular weight of the dibenzoyl peroxide are 0.87 g/cm^3 and 250 g/mole. Termination occurs only by combination. The rate constants are:

k_d = 3.0×10^{-6} s^{-1}

k_p = 1.0×10^{3} L mol.$^{-1}$ s^{-1}

k_t = 3.0×10^{7} L mol.$^{-1}$ s^{-1}

initiator efficiency, f = 0.4

3.1 Calculate the steady-state concentration of free radicals.

3.2 Calculate $\overline{M}_n$ of the polymer formed.

3.3 Calculate the amount of polymer formed in the first 5 hours of reaction.

3.4 If there is chain transfer to monomer also occurs in the reaction suggest how you would estimate the $\overline{M}_n$.

Note that:

$$\text{initiator half life} = \frac{\ln 2}{k_d}$$

$$-\frac{d[M]}{dt} = \frac{k_p}{k_t^{1/2}} (f k_d [I])^{1/2} [M]$$

$$-\ln \frac{[M]}{[M]_o} = \frac{k_p}{k_t^{1/2}} (f.k_d [I])^{1/2} . t$$

$$\nu = \frac{k_p [M]}{2 (f k_d k_t [I])^{1/2}}$$

(25 marks)

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4. a) Would you expect the glass-transition temperatures of polymethyl methacrylate and natural rubber to be higher or lower than room temperature? Why?

(2 marks)

b) Explain the effect of temperature on the kinetic chin length in a free radical chain polymerization.

(2 marks)

c) What is the effect of chain transfer on molecular weight and molecular weight distribution in chain polymerization?

(2 marks)

d) Why is chain transfer to solvent more important than chain transfer to initiator in a free radical reaction?

(2 marks)

e) Explain the effect of temperature on rate of anionic polymerization.

(2 marks)

f) Write schematic reactions and an expression for $\bar{x}_n$ of cationic polymerization.

(4 marks)

g) Why block copolymers can not be formed by free radical polymerization?

(2 marks)

h) A pair of monomers M_1 and M_2 forms an azeotropic copomer at $f_1 = 0.4$. Explain how you would estimate the copolymer composition formed at the reaction time of 1 second and another composition formed at 1 hour later if the feed composition f_1 is 0.2.

(4 marks)

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5. Vinyl acetate (monomer 1) at 3.5 mol. L^{-1} and vinyl chloride (monomer 2) at 1.5 mol. L^{-1} concentration are copolymerized in the reactor at 60°C in benzene solution. The free radical reaction is initiated by adding 0.1 mol. L^{-1} of azobisisobutyronitrile. The reactivity ratios are $r_1 = 0.23$ and $r_2 = 1.68$.

   5.1 Plot F_1 vs. f_1 on the provided graph on page 14. What is the copolymer structure?

   5.2 Calculate the copolymer composition (in mole percent) formed at an early stage of the reaction.

   5.3 Will a composition drift occur? Why?

   5.4 If the average length of M_1 in the copolymer, $\overline{m}_{M_1}$, is the average number of M_1 in each same repeating M_1, calculate $\overline{m}_{M_1}$.

   Would you expect the average length of M_2 in the copolymer, $\overline{m}_{M_2}$, to be longer or shorter than $\overline{m}_{M_1}$? Why?

   Note that:

   average length of M_1 in the copolymer $= \overline{m}_{M_1} = 1 + r_1 \frac{[M_1]}{[M_2]}$

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]\,(r_1\,[M_1] + [M_2])}{[M_2]\,([M_1] + r_2\,[M_2])}$$

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}$$

$$(f_1)_c = \frac{1 - r_2}{2 - r_1 - r_2}$$

(25 marks)

End of Question

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Answer to Q5.

Graph paper for Question (5.1)